

## 9. EFFECTS ON MATERIALS



The deposition of airborne particles on the surface of building materials and culturally important articles (e.g., statuary) can cause damage and soiling, thus reducing the life usefulness and aesthetic appeal of such structures (National Research Council, 1979; Baedecker et al., 1991). Furthermore, the presence of particles on surfaces may also exacerbate the physical and chemical degradation of materials that normally occur when these materials are exposed to environmental factors such as wind, sun, temperature fluctuations, and moisture. Beyond these effects, particles, whether suspended in the atmosphere, or already deposited on a surface, also adsorb or absorb acidic gases from other pollutants like sulfur dioxide ( $\text{SO}_2$ ) and nitrogen dioxide ( $\text{NO}_2$ ), thus serving as nucleation sites for these gases. The deposition of "acidified" particles on a susceptible material surface is capable of accelerating chemical degradation of the material. Therefore, concerns about effects of particles on materials are relate both to impacts on aesthetic appeal and physical damage to material surfaces, both of which may have serious economic consequences. Insufficient data are available regarding perception thresholds with respect to pollutant concentration, particle size, and chemical composition to determine the relative roles these factors play in contributing to materials damage.

This chapter briefly discusses the effects of particle exposure on the aesthetic appeal and physical damage to different types of building materials. This chapter also discusses the effects of dry deposition of acid forming gases on economically important materials. For more detailed discussion of the effects of acid gases on materials, see the 1991 National Acid Precipitation Assessment Program report (Baedecker et al., 1991).

### 9.1 CORROSION AND EROSION

#### 9.1.1 Factors Affecting Metal Corrosion

The mechanisms controlling atmospheric corrosion of metals have been thoroughly discussed in the National Acid Precipitation Assessment Program (Baedecker et al., 1991). In summary, metals undergo corrosion in the absence of pollutant exposure through a series of physical, chemical, and biological interactions involving moisture, temperature, oxygen, and

various types of biological agents. In addition to these environmental factors, atmospheric pollutant exposure may accelerate the corrosion process. Pollutant-induced corrosion arises from complex interactions of the pollutant with the metal surface and the metal corrosion film. In the absence of moisture, there would be limited pollutant-induced or nonpollutant-induced corrosion.

The atmospheric corrosion of most metals is a diffusion-controlled electrochemical process. For an electrochemical reaction to take place, there must exist an electromotive force between points on the metal surface; a mechanism for charge transfer between the electronic conductors; and a conduction path between the cathode and anode reaction centers (Haynie, 1980). The rate of corrosion is still, however, dependent upon the deposition rate and nature of the pollutant (discussed in Chapter 3 of this document); the variability in the electrochemical reactions; the influence of the metal protective corrosion film; the effects of the pollutant coupled with the amount of moisture present (time-of-wetness; relative humidity) (Zhang et al., 1993; Pitchford and McMurry, 1994; Li et al., 1993); the presence and concentration of other surface electrolytes; and the orientation of the metal surface.

The principal form of atmospheric metal corrosion is the uniform corrosion of the metal surface. Other forms of corrosion include pitting, grain-boundary corrosion, and stress-corrosion cracking.

#### **9.1.1.1 Moisture**

The formation of a moisture layer (condensation) on the metal surface is dependent upon precipitation in the form of rain, fog, mist, thawing snow and sleet, and dew. The moisture layer provides a medium for conductive paths for electrochemical reactions and a medium for water soluble air pollutants.

A moisture layer may also form as the result of the reaction of adsorbed water with the metal surface or protective corrosion film, deposited particles and salts from the reaction of the metal surface, and deposited particles with reactive gases. Of particular importance is the production of hydrated corrosion products that increase the absorption rate of moisture. The presence of these hygroscopic salts can drastically decrease the critical relative humidity, resulting in large amounts of moisture on the metal surface.

When the temperature of a metal is below the ambient dew point, water condenses on the metal surface. Whether or not the metal reaches the temperature at which condensation occurs varies with heat transfer between ground and metal and between air and metal. Condensation occurs when the relative humidity adjacent to the surface exceeds a value in equilibrium with the vapor pressure of a saturated solution of whatever salts are on the surface. The solution may contain corrosion products, other hygroscopic contaminants, or both. Temperature, wind, sunshine, and night sky cover then become factors in establishing corrosion rates, since they determine whether there will be sufficient dew condensation.

The first evidence of ambient relative humidity-dependent atmospheric corrosion was demonstrated by Vernon (1931, 1935). Vernon showed a dramatic increase in weight gain in magnesium and iron samples when the relative humidity exceeded certain values (critical relative humidities) in the presence of  $\text{SO}_2$ . More recently, researchers have shown particle size related effects based on relative humidity (Pitchford and McMurtry, 1994). A more detailed discussion on the water content of atmospheric aerosols and its dependence on relative humidity appears in Chapter 3 of this document.

According to Schwartz (1972), the corrosion rate of a metal could increase by 20% for each increase of 1% in the relative humidity above the critical relative humidity value. It is evident that relative humidity has a considerable influence on the corrosion rate, as established in laboratory trials by Haynie and Upham (1974) and Sydberger and Ericsson (1977). Although these experimental results do not support the exact rate predicted by Schwartz (1972), they do indicate that the corrosion rate of steel increases with increasing relative humidity.

Since average relative humidity is calculated from the relative humidity distribution, an empirical relationship exists between average relative humidity and the fraction of time some "critical humidity value" (minimum concentration of water vapor required for corrosion to proceed) is exceeded, assuming a relatively constant standard deviation of relative humidity (Mansfeld and Kenkel, 1976; Sereda, 1974). The fraction of time that the surface is wet must be zero when the average relative humidity is zero and unity when the average relative humidity is 100%. According to Haynie (1980), the following equation is the simplest single-constant first-order curve that can be fitted to observed data:

$$f = (1 - k)/(100 - k)RH \quad (9-1)$$

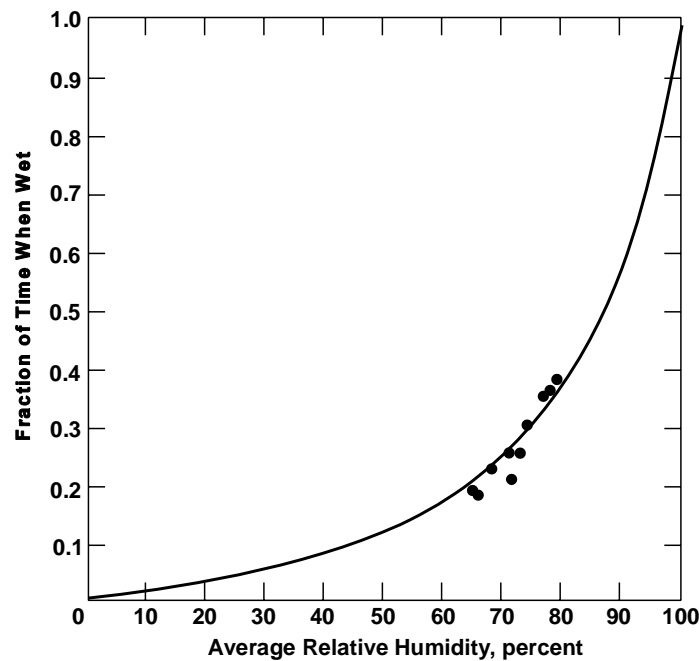
where

$f$  = fraction of time relative humidity exceeds the critical value,

$RH$  = average relative humidity, and

$k$  = an empirical constant less than unity.

Haynie (1980) analyzed and fitted, by the least-squares method, ten quarter-year periods of relative humidity data from St. Louis International Airport to this equation. The fraction of time the relative humidity exceeded 90% gave a value of 0.86 for  $k$ . This fraction and the data points are plotted in Figure 9-1.



**Figure 9-1. Empirical relationship between average relative humidity and fraction of time when a zinc sheet specimen is wet.**

Source: Haynie (1980).

### ***Time-of-Wetness Sensors***

Time-of-wetness sensors, sensors that detect moisture using an electrochemical cell, have been developed to better determine critical relative humidities. The first of these

sensors, developed by Sereda (1958) and Tomashov (1966), measured voltage and current changes across galvanic cells. More recently, Mansfeld and Vijaykumar (1988) reported a technique that uses single metal electrodes for detection of moisture and measurement of the corrosion rate.

Haynie and Stiles (1992) evaluated the Mansfeld type Atmospheric Corrosion Rate Monitor (ACRM) with 19 mo of exposure in an hourly monitored field environment. Duplicate sensors were exposed each at 30° and 90° C. The distribution of measured currents were bimodal for all sensors with definite minimums at around a cell resistance of  $10^{6.5}$  ohms between wet and dry modes. Thus, the sensors can be used to measure time-of-wetness with good reproducibility between sensors exposed at the same time in the same manner. An analysis of variance of the results revealed statistically significant differences between exposure months and angles but not between sensors. Also, there was a significant interaction between month and exposure angle. From these results it was concluded that the sensors are sensitive enough to detect changes with time that are not associated with the primary effects of surface temperature or air moisture content. The magnitude of the dew point/surface temperature difference when a surface becomes wet changes with time, possibly as corrosion products and pollutant concentrations change on the surface. Exposure angle affects time-of-wetness by changing the surface temperature. The surface temperature is related to the relative sun angle and the angle with respect to the night sky. The angle affects radiant heat transfer. This effect was observed as an interaction between seasonal change and exposure angle. Further analysis of the magnitude of the sensor responses when they were wet and comparing the results with weight loss data and model predictions indicated that they were measuring cell resistance rather than polarization resistance (Haynie and Stiles, 1992).

#### **9.1.1.2 Temperature**

Few recent studies were found on the effects of temperature on the corrosion process, and earlier studies (Guttman and Sereda, 1968; Barton, 1976; Haynie et al., 1976; Guttman, 1968; Haynie and Upham, 1974; Harker et al., 1980) disagree on the role temperature plays in the rate of corrosion. How temperature affects the corrosion rate of metal was probably best explained by Haynie (1980). He reported that the rate of metal corrosion is diffusion-

controlled, and that under normal temperature conditions, effects on the rate of corrosion would likely not be observed. A decrease in temperature would raise the relative humidity but decrease diffusivity. When the temperature reaches freezing, a decrease in the overall corrosion rate occurs because diffusion has to take place through a solid (Haynie, 1980; Bieffer, 1981; Sereda, 1974). Available recent studies on the effects of temperature on metal corrosion are discussed below in various subsections on pollutant-induced corrosion of various specific metals.

#### **9.1.1.3 Formation of a Protective Film**

The rust layer on steel is somewhat protective against further corrosion, though far less so than the corrosion layer on zinc and copper. The content of soluble compounds in rust limits its protection of steel. Rust samples analyzed by Chandler and Kilcullen (1968) and Stanners (1970) contained 2 to 2.5% soluble  $\text{SO}_4^{2-}$  and 3 to 6% total  $\text{SO}_4^{2-}$ . The outer rust layer contained a small amount (0.04 to 0.2%) of soluble  $\text{SO}_4^{2-}$ , compared with 2% in the inner rust layer. The concentration of insoluble  $\text{SO}_4^{2-}$  was fairly uniform throughout the rust layers.

The composition of the rust layer has led to studies of the corrosion protective properties of rust as a function of exposure pattern (Nriagu, 1978; Sydberger, 1976). Steel samples initially exposed to low concentrations of sulfur oxides ( $\text{SO}_x$ ) and then moved to sites of higher  $\text{SO}_x$  concentrations corroded at a slower rate than did samples continuously exposed to the higher concentrations. Exposure tests started in summer showed slower corrosion rates during the first years of exposure than those started in winter.

The long-term corrosion rate of steel appears to depend on changes in the composition and structure of the rust layer. During the initiation period, which varies with the  $\text{SO}_2$  concentration and other accelerating factors, the rate of corrosion increases with time (Barton, 1976). Because it is porous and non-adherent, the rust initially formed offers no protection and may accelerate corrosion by retaining hygroscopic sulfates and chlorides, producing a micro-environment with a high moisture content. This is consistent with the concept of sulfate nests discussed by Kucera and Mattsson (1987). After the initiation stage, the corrosion rate decreases as the protective properties of the rust layer improve. Satake and Moroishi (1974) relate this slowing down to a decrease in the porosity of the rust layer.

During a third and final stage, corrosion attains a constant rate and the amount of  $\text{SO}_4^{2-}$  in rust is proportional to atmospheric  $\text{SO}_2$  concentrations. The quantitative determination and subsequent interpretation of corrosion rates becomes difficult if it is not known how long the metal has had a surface layer of electrolyte. Variations in the "wet states" occur with relative humidity, temperature, rain, dew, fog, evaporation, wind, and surface orientation. Capillary condensation in rust can be related to the minimum atmospheric moisture content that allows corrosion to occur (i.e., critical relative humidity). Centers of capillary condensation of moisture on metals can occur in cracks, on dust particles on the metal surface, and in the pores of the rust (Tomashov, 1966).

### 9.1.2 Development of a Generic Dose-Response Function

There are several factors that are important in the corrosion process. First, the rate of corrosion is decreased in the absence of moisture (moisture layer). Secondly, the deposition rate of a pollutant is more important in determining the rate of corrosion than the pollutant concentration. Lastly, the protective corrosion layer may be affected by either dry or wet deposition. A generic semi-theoretical model has been developed that takes into account these factors (Edney et al., 1986; Haynie, 1988; Haynie et al., 1990; and Spence et al., 1992). The model is based on the relative rates of the competing processes of buildup and dissolution of protective corrosion product films. It is a mathematical function that expresses the relationship between corrosion and environmental factors. The general form of the equation is:

$$C = bt_w + a/(Dc/dt_w) \quad (9-2)$$

or a transcendental form:

$$C = bt_w + a(1 - \exp[-Bc/a])/b \quad (9-3)$$

where  $C$  is the amount of corrosion,  $t_w$  is time-of-wetness,  $a$  is a film diffusivity term, and  $b$  is a film dissolution rate. The last two terms are associated with the conditions of the environment and the corrosion product film. For long-term exposures, the exponential term approaches zero and the film reaches a steady state thickness. The equation simplifies to the linear form:

$$C = bt_w + a/b. \quad (9-4)$$

It is in determining the magnitude of the term  $b$  that the effects of pollution on corrosion can be analyzed. More detailed discussion of a generic dose-response function comparing metal corrosion in the absence of pollution and acidic dry deposition of acidic aerosols appears in Baedecker et al. (1991).

### 9.1.3 Studies on Metals

#### 9.1.3.1 Acid-Forming Aerosols

##### *Ferrous Metals*

Ferrous metals include iron, steel, and steel alloys. Stainless steels, incorporating chromium, molybdenum, and nickel, are highly corrosion resistant because of the protective properties of the oxide corrosion film; however, in more polluted areas, the oxide corrosion film becomes less protective. Based on early studies, reported in the National Acid Precipitation Assessment Program report (Baedecker et al., 1991), most steels are susceptible to corrosion from pollutant exposure unless covered by an organic or metallic covering. The rate of corrosion was related to the amount of  $SO_2$  in the atmosphere, showing increasing rates of corrosion with increasing concentrations of  $SO_2$ . The rate of corrosion was also found to depend on the deposition rate of  $SO_2$ .

A recent report by Butlin et al. (1992a) also demonstrated that the corrosion of mild steel and galvanized steel was  $SO_2$ -dependent. These researchers monitored the corrosion of steel samples by  $SO_2$  and ozone ( $O_3$ ) under artificially fumigated environmental conditions, and  $NO_2$  under natural conditions. The natural meteorological conditions of the areas were unaltered. Annual average  $SO_2$  concentrations ranged from  $2.1 \mu g/m^3$  in a rural area to  $60 \mu g/m^3$  in one of the  $SO_2$ -fumigated locations. Annual average  $NO_2$  concentrations ranged from  $1.5 \mu g/m^3$  in the most rural area to  $61.8 \mu g/m^3$  in the most polluted area. They found that corrosion of the steel samples was more dependent on the long-term  $SO_2$  concentration and was only minimally affected by nitrogen oxides ( $NO_x$ ).



### ***Aluminum and Aluminum Alloys***

Aluminum is generally considered corrosion resistant, but when exposed to very high SO<sub>2</sub> concentrations and relative humidities above 50%, aluminum will corrode rapidly, forming a hydrated aluminum sulfate. When aluminum is exposed to low concentrations of acid sulfate particles, a protective aluminum oxide film is formed.

Early evaluations of the effects of SO<sub>2</sub> exposure on aluminum indicated that corrosion of aluminum by SO<sub>2</sub> was exposure-dependent and insignificant, based on loss of metal thickness (Haynie, 1976; Fink et al., 1971). However, Haynie (1976) reported SO<sub>2</sub> exposure-related loss in bending strength in the aluminum samples.

In a more recent study, Butlin et al. (1992a) reported that aluminum corrosion was insignificant in SO<sub>2</sub>-spiked environments. The aluminum samples were exposed under natural environmental conditions (29 sites) for up to 2 years. The corrosion was greater and often more patchy on the underside of some of the metal samples. The authors attributed the increased corrosion on the underside of some samples to the lack of pollutant washoff by rain and an increased concentration of particulate matter (dust) in those test areas.

Aluminum alloy 3003-H14 was exposed to various acid forming aerosols and particles as part of the National Acid Precipitation Assessment Program (Baedecker et al., 1991). Aluminum samples were exposed at 5 sites (Newcomb, NY, Chester, NJ, Washington, DC, Steubenville, OH, and Research Triangle Park, NC). Corrosion after 60 mo of exposure, as measured by weight loss, was more than three times greater at the industrial site (NJ) than at rural sites. Particulate matter concentrations ranged from 14 µg/m<sup>3</sup> in NY to 60 µg/m<sup>3</sup> in OH and DC. The concentration ranges for other pollutants at the 5 sites appears in Table 9-1. Even at the industrial site the corrosion rate was very low at a factor of about 10 less than for Galvalume (aluminum-zinc). The exposure time and the average corrosion rate by site is listed in Table 9-2.

### ***Copper and Copper Alloys***

Graedel et al. (1987) studied the chemical composition of patinas exposed in the greater New York area for from 1 to 100 years and compared the results with estimated dry and wet deposition of pollutants between 1886 and 1983. They concluded that the long-term corrosion of copper was not controlled by deposition of pollutants, but rather, it was more

**TABLE 9-1. ANNUAL AVERAGE AND MAXIMUM VALUES OF THE HOURLY AVERAGES FOR SULFUR DIOXIDE (SO<sub>2</sub>), NITROGEN OXIDE (NO<sub>x</sub>), AND OZONE (O<sub>3</sub>) AND ANNUAL AVERAGES OF THE MONTHLY AVERAGES OF RAIN pH AT THE FIVE MATERIAL EXPOSURE SITES, BASED ON DATA ACQUIRED DURING 1986<sup>a</sup>**

Site	SO <sub>2</sub> (ppb)		NO <sub>2</sub> (ppb)		O <sub>3</sub> (ppb)		Particulate Matter (μg/m <sup>3</sup> )	
	Avg.	Max.	Avg.	Max.	Avg.	Max.	Avg.	Avg.
NC	2±4	45	14±9	65	25±21	99	35	4.33
DC	12±9	91	28±12	91	17±16	99	60	4.10
NJ	6±7	87	14±10	98	30±20	114	30	4.16
NY	2±3	29	2±2	21	30±14	99	14	4.28
OH	15±17	450	19±11	98	19±17	94	60	3.90

<sup>a</sup>The ± errors are estimates of one standard deviation on a single hourly average based on the dispersion of the data.

Source: Baedecker et al. (1991).

**TABLE 9-2. AVERAGE CORROSION RATES FOR 3003-H14 ALUMINUM OBTAINED DURING THE NATIONAL ACID PRECIPITATION ASSESSMENT PROGRAM BETWEEN 1982 AND 1987**

Site	Exposure Time (y)	Average Corrosion Rate (μm/y)
NC	5	0.036
DC	5	0.069
NJ	5	0.106
NY	5	0.036
OH	1	0.056

Source: Baedecker et al. (1991).

likely controlled by the availability of copper to react with deposited pollutants. The patina, that is mostly basic sulfate, is not readily dissolved by acids and thus provides significant protection for the substrate metal. However, according to Simpson and Horrobin (1970), the formation of these basic copper salts can take as long as 5 or more years and will vary with the concentration of SO<sub>2</sub> or chloride particles, the humidity, and the temperature.

Butlin et al. (1992a) reported an average rate for copper corrosion of  $1 \pm 0.2 \mu\text{m/y}$  in 19 of 29 sites evaluated. In areas where there was above average  $\text{SO}_2$ , mass loss ranged from 1.5 to  $1.75 \mu\text{m/y}$ . The lowest recorded mass loss was  $0.66 \mu\text{m/y}$  in an area with low precipitation and low  $\text{SO}_2$ . The maximum pit depth over a 2-year period was  $63 \mu\text{m}$ .

Meakin et al. (1992) reported on the atmospheric degradation of monumental bronzes. They measured ion concentrations in rain run off from brigade markers at the Gettysburg National Military Park as well as rain samples. There was a very strong correlation between copper and sulfate ions with a regression coefficient not significantly different from the stoichiometric value for cupric sulfate. There appeared to be little correlation between the acidity of the run off and the acidity of the rain fall on the markers. Dry deposition between rain events was concluded to dominate the soluble corrosion of the bronze.

Because of the complexity of the patina formation, few damage functions have been reported and most of those that have been reported were based on short-term data when the patina had not developed. Corrosion rates of  $0.5$  to  $1 \mu\text{m/y}$  have been predicted by these equations. However, the values greatly over estimate long-term damage and would be misleading in an economic assessment.

Although limited to 5 years of exposure, the National Acid Precipitation Assessment Program study (Baedecker et al., 1991; Cramer et al., 1989) may be useful in evaluating the affects of  $\text{SO}_2$  on copper because it analyzed 110 Cu soluble corrosion data with components of the previously discussed generic damage function. The average total corrosion rate between 3 and 5 years was about  $1 \mu\text{m/y}$  but the soluble portion was less than a third of that which could be statistically attributed to  $\text{SO}_2$ . The resulting coefficient for the product of  $\text{SO}_2$  times the time-of-wetness was  $0.18 \text{ cm/s}$  which has the units of a deposition velocity. This term may be multiplied by a stoichiometric conversion factor to get a corrosion rate. With  $\text{SO}_2$  expressed in  $\text{mg/m}^3$  and time-of-wetness in years, the conversion factor for  $\mu\text{m/y}$  of Cu to cupric sulfate is 0.035. The coefficient is 0.0063 and for an average concentration of  $20 \text{ mg/m}^3$  of  $\text{SO}_2$  the resulting corrosion rate is  $0.126 \mu\text{m/y}$  of wetness. If the surface is wet only a quarter of the time, the corrosion rate attributable to  $\text{SO}_2$  is around  $0.03 \mu\text{m/y}$ . If the patina color has aesthetic value, and  $\text{SO}_2$  accelerates the formation, then, in the case of Cu, the presence of  $\text{SO}_2$  may be beneficial.

### ***Zinc and Galvanized Steel***

In the presence of moisture and oxygen, zinc will form an initial corrosion product of zinc hydroxide. Carbon dioxide ( $\text{CO}_2$ ) in the atmosphere further reacts with this film to form basic zinc carbonates. This corrosion product is insoluble in neutral environments but dissolves in both strong acids and strong bases. Zinc is electrochemically more active than iron. Coating steel with zinc provides a protection to the steel substrate against atmospheric corrosion.

Many studies conducted on the corrosive properties of zinc and zinc products are extensively evaluated in the National Acid Precipitation Assessment Program report (Baedecker et al., 1991). Two of the studies, conducted over a 20-year period, showed zinc corrosion rates of 0.22 to 7.85  $\mu\text{m/y}$  from 1931 to 1951 and 0.6 to 3.6  $\mu\text{m/y}$  from 1957 to 1977 (Anderson, 1956; Showak and Dunbar, 1982). State College, PA was the only site common to both studies. The corrosion rates were 1.13 and 1.2  $\mu\text{m/y}$ .

Harker et al. (1980) examined the variables controlling the corrosion of zinc by  $\text{SO}_2$  and sulfuric acid ( $\text{H}_2\text{SO}_4$ ). Experimental conditions were selected from the following ranges:

Temperature	12 to 20 °C
Relative humidity	65 to 100%
Mean flow velocity	0.5 to 8 m/s
Sulfur dioxide concentration	46 to 216 ppb
Sulfate aerosol mass concentration	1.2 $\text{mg/m}^3$
Aerosol size distribution	0.1 to 1.0 $\mu\text{m}$

The factors controlling the rate of corrosion were found to be relative humidity, pollutant flux, and the chemical form of the pollutant. Corrosion occurred only when the relative humidity was greater than 60%. The deposition velocities were 0.07 cm/s for 0.1 to 1.0 ppm  $\text{H}_2\text{SO}_4$  aerosols and 0.93 cm/s for  $\text{SO}_2$  at a friction velocity of 35 cm/s. The results indicate that  $\text{SO}_2$ -induced corrosion of zinc proceeds at a rate approximately a factor of two greater than that for the equivalent amount of deposited  $\text{H}_2\text{SO}_4$  aerosol. Temperature did not appear to be a controlling factor within the range 12 to 20 °C.

Edney et al. (1986) conducted controlled environmental chamber experiments on unexposed galvanized steel panels to determine the rate at which  $\text{SO}_2$  deposits to fresh test panels and the fate of the deposited compound. During exposure, dew was periodically produced on some of the panels. After exposure, samples were washed with sprays of different pH levels to simulate acidic wet deposition. The runoff samples were analyzed for corrosion product ions.

In the absence of dew, deposited  $\text{SO}_2$  was absorbed. With dew present, the absorption rate increased substantially. At a chamber flow rate of 3 m/s, the flux of  $\text{SO}_2$  to the panel surfaces was directly proportional to the air concentration and the regression slope represents a deposition velocity of 0.9 cm/s. A linear regression slope between zinc and sulfate in the runoff was 1.06, which is consistent with a stoichiometric reaction.

The National Acid Precipitation Assessment Program (Baedecker et al., 1991; Cramer et al., 1989) included zinc and galvanized steel panels in its field exposure experiments in Newcomb, NY, Newark, NJ, Washington, DC, Research Triangle Park, NC, and Steubenville, OH. The NC and OH sites were the only two of the 5 sites that had covers and spray devices set up to separate the effects of wet and dry deposition of pollutants. Air quality, meteorological parameters, and rain chemistry were determined at all sites. Runoff samples were collected and analyzed for both ambient rain and the deionized water spray.

In general, the rolled zinc corrosion rates were larger than those found for the galvanized steel panels, most likely because of a protective chromate treatment that had been factory applied to the galvanized steel. The deposition of  $\text{SO}_2$  was one of several corrosion contributing factors. The concentrations of  $\text{SO}_2$  at the different sites varied by as much as a factor of 10, but the corrosion rates were within a factor of 2 (see Table 9-3). Pollutant concentrations at the 5 exposure sites appear in Table 9-1.

At the NC and OH sites, exposed samples of both zinc and galvanized steel corroded more than similar samples exposed to the clean simulated rain. Although  $\text{SO}_2$  levels were higher at the OH site, the deionized water spray samples corroded about the same at both sites. This result, together with high levels of particles at the industrial OH site, may indicate that much of the deposited  $\text{SO}_2$  was neutralized by dry deposited alkaline particles.

Cramer et al. (1989) did a preliminary analysis of the soluble fraction of the total zinc corrosion with respect to the model of the generic damage function. The multiple regression

**TABLE 9-3. AVERAGE CORROSION RATES FOR ROLLED ZINC AND GALVANIZED STEEL OBTAINED DURING THE NATIONAL ACID PRECIPITATION ASSESSMENT PROGRAM FIELD EXPERIMENTS**

Site	Exposure Time (y)	Average Corrosion Rate ( $\mu\text{m/y}$ )	
		Rolled Zinc	Galvanized Steel
NC	5	0.81	0.73
DC	5	1.27	0.71
NJ	5	1.32	0.99
NY	5	0.63	0.63
OH	1	1.33	0.99

Source: Baedecker et al. (1991)

analysis gave significant coefficients for  $\text{SO}_2$ , hydrogen ions ( $\text{H}^+$ ), and  $\text{CO}_2$  in precipitation. The coefficient for  $\text{SO}_2$  was not significantly different from stoichiometric for both the rolled zinc and the chromated galvanized steel. Most of the zinc corrosion product was soluble. Haynie et al. (1990) have calculated the solubility of basic zinc carbonate in equilibrium with water containing  $\text{CO}_2$ . Zinc solubility is very temperature dependent due to the strong inverse dependence of  $\text{CO}_2$  solubility in water, leading to increased dissolution of the corrosion products as the ambient temperature decreases.

In the study reported by Butlin et al. (1992a), galvanized steel was found to corrode at a rate of  $1.45 \mu\text{m/y}$  (high precipitation, low  $\text{SO}_2$ ) to  $4.25 \mu\text{m/y}$  (high  $\text{SO}_2$ ). Galvanized steel samples from the area of low rainfall and low  $\text{SO}_2$  had a corrosion rate of  $1.53 \mu\text{m/y}$ . Metallographical evaluation of the galvanized steel samples showed only superficial corrosion with no penetration of the zinc coating.

The various factors that contribute to the corrosion of zinc and galvanized steel are discussed in more detail in terms of the model of the generic damage function in Spence and Haynie (1990), Haynie et al. (1990), and Spence et al. (1992). The combined terms of the long-term form of the model are:

$$\mathbf{C} = \mathbf{F} + \mathbf{C}_d + \mathbf{C}_{RA} + \mathbf{C}_{RC} \quad (9-5)$$

where  $C$  is total corrosion in  $\mu\text{m}$ ,  $F$  is the equivalent thickness of zinc remaining in the insoluble corrosion product film and, at steady state, is equal to  $a/b$ ,  $C_d$  is the corrosion

associated with deposition of SO<sub>2</sub> both in wet and dry periods, and C<sub>RC</sub> is the corrosion due to rain acidity (H<sup>+</sup> and dissolved CO<sub>2</sub>). The SO<sub>2</sub> contribution, C<sub>d</sub>, is expressed as follows:

$$C_d = 0.045 V_d(SO_2)t_w + 1.29 \times 10^{-4} A_r N \quad (9-6)$$

where,

C<sub>d</sub> = zinc corrosion, μm

V<sub>d</sub> = deposition velocity (wind speed, shape, and size dependent), cm/s

SO<sub>2</sub> = ambient SO<sub>2</sub> concentration, mg/m<sup>3</sup>.

A<sub>r</sub> = ratio of actual to apparent surface area

N = number of times surface is dry during the exposure period.

The first additive term represents corrosion from the dry deposition of SO<sub>2</sub> during periods of wetness caused by condensation (dew), and the second term is the corrosion associated with the adsorption of a monolayer of SO<sub>2</sub> during periods of dryness.

In the absence of sufficient data to accurately determine each of the terms, Haynie et al. (1990), and Spence et al. (1992) have applied assumed values for flat galvanized specimens (different sizes), large sheets, and wire with reasonable success. More recently, Cramer and Baker (1993) have applied the generic damage function to predict the expected life of the restored tin plated roof of Monticello. Thus, the model can be used to assess the economic effects of atmospheric corrosion on several metals, especially zinc.

### 9.1.3.2 Particles

Only limited information is available on the effects of particles alone on metals. Goodwin et al. (1969) reported damage to steel, protected with a nylon screen, exposed to quartz particles. The damage did not, however, become substantial until the particle size exceeded 5 μm. Barton (1958) found that dust contributed to the early stages of metal corrosion. The effect of dust was lessened as the rust layer formed. Other early studies also indicated that suspended particles can play a significant role in metal corrosion. Sanyal and Singhania (1956) wrote that particles, along with other cofactors and SO<sub>2</sub>, promoted the corrosion of metals in India. Yocom and Grappone (1976) and Johnson et al. (1977) reported that moist air containing both particles and SO<sub>2</sub> resulted in a more rapid corrosion rate than air polluted with SO<sub>2</sub> alone. Russell (1976) stated that particles serve as points for

the concentration of active ionic species on electrical contact surfaces, thereby increasing the corrosion rate of  $\text{SO}_x$ . However, other studies have not established a conclusive statistical correlation between total suspended particulates (TSP) and corrosion, possibly due to data limitations (Mansfeld, 1980; Haynie and Upham, 1974; and Upham, 1967; Yocom and Upham, 1977).

Edney et al. (1989) reported on the effects of particles,  $\text{SO}_2$ ,  $\text{NO}_x$ , and  $\text{O}_3$  on galvanized steel panels exposed under actual field conditions in Research Triangle Park, NC, and Steubenville, OH, between April 25 and December 28, 1987. The panels were exposed under the following conditions: (1) dry deposition only; (2) dry plus ambient wet deposition; and (3) dry deposition plus deionized water. The average concentrations for  $\text{SO}_2$  (in ppb) and particulate matter (in  $\mu\text{g}/\text{m}^3$ ) was 22 ppb and  $70 \mu\text{g}/\text{m}^3$  and  $<1$  ppb and  $32 \mu\text{g}/\text{m}^3$  for Steubenville and Research Triangle Park, respectively. By analyzing the runoff from the steel panel the authors concluded that the dissolution of the steel corrosion products for both sites was likely the result of deposited gas phase  $\text{SO}_2$  on the metal surface and not particulate sulfate.

Dean and Anthony (1988) investigated the atmospheric corrosion of unstressed wrought aluminum alloys at three sites representing industrial, marine, and coastal-industrial environments. After 10 years of exposure, degradation was measured by several means. They reached the following conclusions: (1) a sooty industrial environment is far more damaging than a warm, salt-laden seacoast atmosphere, (2) by far the most noticeable effect of prolonged atmospheric exposure is loss of ductility in susceptible alloys, and (3) sacrificial cladding completely eliminates ductility loss.

Walton et al. (1982) performed a laboratory study of the direct and synergistic effects of different types of particles and  $\text{SO}_x$  on the corrosion of aluminum, iron, and zinc. The four most aggressive species were salt and salt/sand from marine or deiced locations, ash from iron smelters, ash from municipal incinerators, and coal mine dusts. Fly ashes of various types were less aggressive. Coal ash with  $\text{SO}_x$  did promote corrosion but oil fly ash was relatively noncorrosive. This suggests that catalytic species in the ash promote the oxidation of  $\text{SO}_x$  and the presence of  $\text{SO}_x$  alone is not sufficient to accelerate corrosion. Other laboratory studies of metal corrosion provide considerable evidence that the catalytic effect is not significant and that atmospheric corrosion rates are dependent on the



conductance of the thin-film surface electrolyte and that the first-order effect of contaminant particles is to increase solution conductance, and, hence corrosion rates (Skerry et al., 1988a,b; Askey et al., 1993).

#### **9.1.4 Paints**

Paints, opaque film coatings, are by far the dominant class of manmade materials exposed to air pollutants in both indoor and outdoor environments. Paints are used as decorative coverings and protective coatings against environmental elements on a variety of finishes including woods, metals, cement, asphalt, etc.

Paints primarily consists of two components: the film forming component and the pigments. Paints undergo natural weathering processes from exposure to environmental factors such as sunlight (ultraviolet light), moisture, fungi, and varying temperatures. In addition to the natural weathering from exposure to environmental factors, evidence exists that demonstrates pollutants affect the durability of paint (National Research Council, 1979).

Paint failure may be manifested by two general degradation modes. The first involves the paint surface and includes paint discoloration, chalking, loss of gloss, and erosion. Paint erosion can be measured by loss of thickness of the paint layer. The second is degradation at the paint/substrate interface, which can be manifested as loss of adhesion leading to blistering and peeling.

In paint formulas, the ratio of pigments to film formers is important to the overall properties of gloss, hardness, and permeability to water. If the amount of film former is too low, soiling is increased and the paint may lose the film flexibility needed for durability and become brittle.

##### **9.1.4.1 Acid-Forming Aerosols**

Paint films permeable to water are also susceptible to penetration by  $\text{SO}_2$  and  $\text{SO}_4^{2-}$  aerosols. Baedecker et al. (1991) reviewed about twenty papers (1958 to 1985) dealing with solubility and permeability of  $\text{SO}_2$  in paints and polymer films. Permeation and adsorption rates varied by as much as several orders of magnitude depending on formulation. They concluded that unpigmented polymer films have a large range of permeabilities but that the polymers used in paint formulations generally do not form barriers to  $\text{SO}_2$  either in the

gaseous state or in solution as sulfurous acid. Although 20% of the absorbed  $\text{SO}_2$  was retained in alkyd/melamine and epoxide films and probably reacted with the polymer, there appears to be little degradation to the polymer itself from  $\text{SO}_2$  at low concentrations. Absorption is inhibited by pigments; those pigments that can catalyze the oxidation of  $\text{SO}_2$  and scavenge the resulting sulfate ions can limit the penetration even more than can typical pigments.

Concentrations of  $\text{SO}_2$  found in fog or near industrial sites can increase the drying and hardening times of certain kinds of paints. Holbrow (1962) found that the drying time of linseed, tung, and certain castor oil paint films increased by 50 to 100% on exposure to 2,620 to 5,240  $\mu\text{g}/\text{m}^3$  (1 to 2 ppm)  $\text{SO}_2$ . The touch-dry and hard-dry times of alkyl and oleoresinous paints with titanium dioxide pigments were also reported to increase substantially; however, the exposure time of the wet films was not reported. Analysis of the dried films indicated that  $\text{SO}_2$  chemically reacted with the drying oils, altering the oxidation-polymerization process. No studies have been reported on the effects of  $\text{SO}_2$  on the drying of latex paints.

Spence et al. (1975) conducted a controlled exposure study to determine the effects of gaseous pollutants on four classes of exterior paints: oil-base house paint, vinyl-acrylic latex house paint, and vinyl and acrylic coil coatings for metals. The house paints were sprayed on aluminum panels. The coil coating panels were cut from commercially painted stock. Recorded paint thickness was oil-base paint film, 58  $\mu\text{m}$ ; acrylic latex, 45  $\mu\text{m}$ ; vinyl coil coating, 27  $\mu\text{m}$ ; and acrylic coil coating, 20  $\mu\text{m}$ . Temperature, humidity, and  $\text{SO}_2$ , (78.6 and 1,310  $\mu\text{g}/\text{m}^3$ ),  $\text{NO}_2$  (94 and 940  $\mu\text{g}/\text{m}^3$ ), and  $\text{O}_3$  (156.8 and 980  $\mu\text{g}/\text{m}^3$ ) exposures were controlled. Each exposure chamber had a xenon arc lamp to provide ultraviolet radiation. A dew/light cycle was included; light exposure time was followed by a dark period during which coolant circulated through racks holding the specimens, thereby forming dew on the panels. Each dew/light cycle lasted 40 min and consisted of 20 min of darkness with formation of dew, followed by 20 min under the xenon arc. The total exposure time was 1,000 h. Damage was measured after 200 h, 500 h, and 1,000 h by loss of both weight and film thickness. In evaluating the data, loss of weight was converted to equivalent loss of film thickness.

Visual examination of the panels coated with oil-base house paint revealed that all exposure conditions caused considerable damage. The erosion rate varied from 28.3 to 79.14  $\mu\text{m}/\text{y}$ , with an average of 60  $\mu\text{m}/\text{y}$ . The investigators concluded that  $\text{SO}_2$  and relative humidity markedly affected the rate of erosion of oil-base house paint. The presence of  $\text{NO}_2$  increased the weight of the paint film. A multiple linear regression on  $\text{SO}_2$  concentration and relative humidity yielded the following relation:

$$E = 14.3 + 0.0151 \text{ SO}_2 + 0.388 \text{ RH} \quad (9-7)$$

where

$E$  = erosion rate in  $\mu\text{m}/\text{y}$ ,

$\text{SO}_2$  = concentration of  $\text{SO}_2$  in  $\mu\text{g}/\text{m}^3$ , and

$\text{RH}$  = relative humidity in percent.

The authors reported the 95% tolerance limits on 99% of the calculated rates to be  $\pm 44 \mu\text{m}/\text{y}$ .

Blisters formed on the acrylic latex house paint at the high  $\text{SO}_2$  levels. The blisters resulted from severe pitting and buildup of aluminum corrosion products on the substrate. The paint acted as a membrane retaining moisture under the surface and excluding oxygen that would passivate the aluminum. The vinyl coating and the acrylic coating are resistant to  $\text{SO}_2$ . The visual appearance of the vinyl coil coating showed no damage. The average erosion rate was low, 3.29  $\mu\text{m}/\text{y}$ . The average erosion rate for a clean air exposure was 1.29  $\mu\text{m}/\text{y}$ . The acrylic coil coating showed an average erosion rate of 0.57  $\mu\text{m}/\text{y}$  (Spence et al., 1975).

A study of the effects of air pollutants on paint, under laboratory controlled conditions, was conducted by Campbell et al. (1974). The paints studied included oil and acrylic latex house paints, a coil coating, automotive refinish, and an alkyd industrial maintenance coating. These coatings were exposed to clean air,  $\text{SO}_2$  at 262 and 2,620  $\mu\text{g}/\text{m}^3$ , and  $\text{O}_3$  at 196 and 1,960  $\mu\text{g}/\text{m}^3$ . Light, temperature, and relative humidity were controlled. In addition, one-half of the coatings were shaded during the laboratory exposures. Similar panels (half facing north) were exposed at field sites in Leeds, ND; Valparaiso, IN; Research Center, Chicago, IL; and Los Angeles, CA.

The laboratory exposure chamber operated on a 2-h light-dew cycle (i.e., 1 h of xenon light at 70% relative humidity and a temperature of 66 °C followed by 1 h of darkness at 100% relative humidity and a temperature of 49 °C). Coating erosion rates were calculated after exposure periods of 400, 700, and 1,000 h. Erosion rates for samples exposed to the lowest exposure concentrations were not significantly different from values for clean air exposures due to the high variability of the data. The erosion rates on the shaded specimens were significantly less than the unshaded panel results; panels facing north were also less eroded. At the highest exposure concentrations, erosion rates were significantly greater than controls for both pollutants, with oil-base house paint experiencing the largest erosion rate increases, latex and coil coatings moderate increases, and the industrial maintenance coating and automotive refinish the smallest increases (Yocom and Grappone, 1976; Yocom and Upham, 1977; and Campbell et al., 1974). Coatings that contained extender pigments, particularly calcium carbonate ( $\text{CaCO}_3$ ), showed the greatest erosion rates from the  $\text{SO}_2$  exposures. Results of field exposures also support these conclusions (Campbell et al., 1974).

Haynie and Spence (1984) evaluated data on two house paints that were exposed for up to 30 mo at 9 environmental monitoring sites in the St. Louis, MO area. The paints were formulated with and without  $\text{CaCO}_3$  and applied to stainless steel panels. Multiple regression analysis of mass loss versus the environmental variables revealed no statistical differences associated with  $\text{SO}_2$ .

Hendricks and Balik (1990) evaluated the effects of  $\text{SO}_2$  on free films of paint and the latex polymer for one of the paints and established diffusion coefficients for  $\text{SO}_2$  in the various formulations. Pigments, as well as fillers such as  $\text{CaCO}_3$ , were found to decrease the diffusion coefficient. A latex polymer desorbed all  $\text{SO}_2$  when placed in a vacuum but an alkyd retained approximately 15 to 20%  $\text{SO}_2$  even after several days. Xu and Balik (1989, 1990) concluded that the gas had reacted with the polymer in the paint. They also determined quantitatively the rate of  $\text{CaCO}_3$  removal from paints exposed to different pH levels of sulfurous acid or distilled water (weak carbonic acid). The rates of dissolution were dependent on acid strength but removal was complete for all acids. The mass loss was 27%. A similar paint without  $\text{CaCO}_3$  lost only 7%.

Patil et al. (1990) reported that certain combinations of  $\text{SO}_2/\text{H}_2\text{O}/\text{UV}$  light (high  $\text{SO}_2$  levels) had detrimental effects when they were evaluating various techniques for measuring

film degradation. Mechanical properties were dominated by cross-linking. While SO<sub>2</sub> had little effect when dry, there was considerable chain scissioning when exposed wet. Sanker et al. (1990) found that after exposing the polymer to SO<sub>2</sub>/UV light that there was a decrease in carbonyl signal associated with the acrylate group, whereas no decrease in carbonyl signal was associated with samples exposed to UV light alone. They reported a synergistic effect on polymer degradation between UV light and SO<sub>2</sub> under both wet and dry conditions.

Edney (1989) and Edney et al. (1988, 1989) measured the chemical composition of runoff from painted red cedar and zinc panels exposed at field sites in Raleigh, NC, and Steubenville, OH, and in controlled chambers. Acidic gases such as SO<sub>2</sub> and nitric acid dissolved alkaline (CaCO<sub>3</sub> or ZnO) components in the paint.

Williams et al. (1987) demonstrated that weathering of wood prior to painting decreases the adhesion of paint. Significant decreases in paint adhesion were noted in panels weathered for 4 weeks and those weathered for 16 weeks had about a 50% decrease in adhesive strength. In similar studies, it was shown that acid treatment of specimens during weathering increased the rate of surface deterioration; the rate of wood weathering increased by as much as 50% when it was exposed to sulfurous, sulfuric, or nitric acids (Williams, 1987, 1988).

As part of the National Acid Precipitation Assessment Program, Davis et al. (1990) studied the effects of SO<sub>2</sub> on oil/alkyd systems on steel using a custom designed exposure chamber in which a dew cycle could be simulated. Energy dispersive X-ray microscopy scans were made across primer/paint cross-sections. Samples were exposed to 1 ppm SO<sub>2</sub> at 90 to 95% relative humidity, and thermally cycled (12-h dew cycle followed by 12-h drying period) or the chamber was maintained at a constant temperature. Controls were exposed under similar conditions but without SO<sub>2</sub>. All samples gained weight after 7 days of exposure. The greatest weight gain was noted in the cyclic samples (30 to 40% more than those samples maintained under constant temperatures). After 28 days to cyclic (dew/drying) conditions samples exposed to SO<sub>2</sub> had rusted scribe marks while the controls showed only light rust.

As the specimens were exposed in the chamber, the tensile strength decreased significantly and the locus of failure shifted from within the coating system to the primer-metal interface. The relationship of tensile strength to metal/primer failure was

approximately linear, suggesting that the decrease in tensile strength was dominated by a loss or weakening of adhesion between the substrate and the primer (Davis et al., 1990).

#### **9.1.4.2 Particles**

Several studies suggest that particles serve as carriers of other more corrosive pollutants, allowing the pollutants to reach the underlying surface or serve as concentration sites for other pollutants (Cowling and Roberts, 1954).

Reports have indicated that particles can damage automobile finishes. In an early study, staining and pitting of automobile finishes was reported in industrial areas. The damage was traced to iron particles emitted for nearby plants (Fochtman and Langer, 1957). General Motors conducted a field test to determine the effect of various meteorological events, the chemical composition of rain and dew, and the ambient air composition during the event, on automotive paint finishes. The study was conducted in Jacksonville, FL. Painted (basecoat/clearcoat technology) steel panels were exposed for varying time periods, under protected and unprotected conditions. Damage to paint finishes appeared as circular, elliptical, or irregular spots, that remained after washing. Using scanning electron microscopy (high magnification) the spots appeared as crater-like deformities in the paint finish. Chemical analyses of the deposit determined calcium sulfate to be the predominant species. It was concluded that calcium sulfate was formed on the paints surface by the reaction of calcium from dust and sulfuric acid contained in rain or dew. The damage to the paint finish increased with increasing days of exposure (Wolff et al., 1990). Table 9-4 contains the atmospheric pollutants and their concentrations during the study.

The formulation of the paint will affect the paint's durability under exposure to varying environmental factors and pollution; however, failure of the paint system results in the need for more frequent repainting and additional cost.

#### **9.1.5 Stone and Concrete**

Air pollutants are known to damage various building stones. Some of the more susceptible stones are the calcareous stones, such as limestone, marble and carbonated cemented stone. The deterioration of inorganic building materials occurs initially through surface weathering. Moisture and salts are considered the most important factors in building

**TABLE 9-4. SUMMARY OF MEASURED PARAMETERS IN  
JACKSONVILLE, FLORIDA  
(Statistics based on 8-h samples)**

Variable	Overall <sup>a</sup>		
	Mean <sup>b</sup>	Standard Deviation	Maximum <sup>c</sup>
Fine particulates <sup>d</sup> ( $\mu\text{g}/\text{m}^3$ )	22.2	11.0	58.2
Particulate matter <sup>e</sup> ( $\mu\text{g}/\text{m}^3$ )	38.7	15.9	89.8
Total suspended particulates ( $\mu\text{g}/\text{m}^3$ )	55.8	22.2	129.2
Fine sulfates <sup>f</sup> ( $\mu\text{g}/\text{m}^3$ )	6.9	4.6	18.1
Sulfates <sup>e</sup> ( $\mu\text{g}/\text{m}^3$ )	7.7	4.9	18.9
Sulfur dioxide ( $\mu\text{g}/\text{m}^3$ )	6.7	9.8	56.6
Fine ammonium ( $\mu\text{g}/\text{m}^3$ )	2.5	1.5	7.8
Fine organic carbon ( $\mu\text{g}/\text{m}^3$ )	2.0	1.3	6.4
Organic carbon <sup>e</sup> ( $\mu\text{g}/\text{m}^3$ )	4.4	2.8	12.9
Fine elemental carbon ( $\mu\text{g}/\text{m}^3$ )	1.3	1.1	5.4
Elemental carbon <sup>e</sup> ( $\mu\text{g}/\text{m}^3$ )	1.8	1.8	8.5
Fine calcium ( $\text{ng}/\text{m}^3$ )	284.0	224.0	1,145.0
Calcium ( $\text{ng}/\text{m}^3$ )	3,572.0	3,850.0	21,073.0
Fine silica ( $\text{ng}/\text{m}^3$ )	132.0	214.0	1,797.0
Silica <sup>e</sup> ( $\text{ng}/\text{m}^3$ )	995.0	909.0	6,572.0
Potassium <sup>e</sup> ( $\text{ng}/\text{m}^3$ )	348.0	140.0	920.0
Titanium <sup>e</sup> ( $\text{ng}/\text{m}^3$ )	42.0	38.0	237.0
Iron <sup>e</sup> ( $\text{ng}/\text{m}^3$ )	421.0	388.0	3,090.0
Total nitrates ( $\mu\text{g}/\text{m}^3$ )	1.3	1.3	8.4
Nitric acid ( $\mu\text{g}/\text{m}^3$ )	0.7	1.2	7.8
Fine nitrates ( $\mu\text{g}/\text{m}^3$ )	0.6	0.3	1.5
Nitrogen oxide (ppb)	3.1	4.0	19.2
Nitrogen dioxide (ppb)	8.8	5.9	32.3
Oxone (maximum) (ppb)	48.0	20.2	93.0

<sup>a</sup>Overall = combination of three daily 8-h samples.

<sup>b</sup>Mean daily ozone maximum.

<sup>c</sup>Maximum ozone concentration over the study period.

<sup>d</sup><2.5  $\mu\text{m}$ .

<sup>e</sup>PM<sub>10</sub> variables.

<sup>f</sup>≤2.5  $\mu\text{m}$ .

Source: Wolff et al. (1990).

material damage. Many researchers believe that the mechanism of damage from air pollution involves the formation of salts from reactions in the stone; subsequently, these surface salts dissolve in moist air and are washed away by rainfall. Luckat (1977) reported good correlation with stone damage and  $\text{SO}_2$  uptake. Riederer (1974) and Niesel (1979) reported that stone damage is predominantly associated with relative humidity  $>65\%$  and freeze/thaw weathering. Still other researchers suggest that microorganisms must also be considered in order to quantify damage to building materials due to ambient pollutant exposure (Winkler, 1966; Riederer, 1974; Krumbein and Lange, 1978; Eckhardt, 1978; Hansen, 1980). Sulfur chemoautotrophs are well known for the damage they can cause to inorganic materials. These microorganisms (e.g., *Thiobacillus*) convert reduced forms of sulfur to  $\text{H}_2\text{SO}_4$  (Anderson, 1978) and the presence of sulfur oxidizing bacteria on exposed monuments has been confirmed (Vero and Sila, 1976). The relative importance of biological, chemical, and physical mechanisms, however, have not been systematically investigated. Thus, damage functions definitely quantifying the relationship of pollutant concentrations to stone and concrete deterioration are not available in the literature.

Baedecker et al. (1991) reviewed the published literature on calcareous stones and concluded that the most significant damage to these stones resulted from the exposure to natural constituents of nonpolluted rain water; carbonic acid from the reaction of  $\text{CO}_2$  with rain reacts with the calcium in the stone. Based on the work conducted by the National Acid Precipitation Assessment Program, 10% of chemical weathering of marble and limestone was caused by wet deposition of hydrogen ions from all acid species. Dry deposition of  $\text{SO}_2$  between rain events caused 5 to 20% of the chemical erosion of stone and the dry deposition of nitric acid was responsible for 2 to 6% of the erosion (Baedecker et al., 1991).

Niesel (1979) completed a literature review on the weathering of building stone in atmospheres containing  $\text{SO}_x$ , which includes references from 1700 to 1979. In summary, he reported that weathering of porous building stone containing lime is generally characterized by accumulation of calcium sulfate dihydrate in the near-surface region. The effect of atmospheric pollutants on the rate of weathering is believed to be predominantly controlled by the stone's permeability and moisture content. Migrating moisture serves primarily as a transport medium. Sulfur dioxide is sorbed and thus can be translocated internally while being oxidized to sulfates. Reacting components of the building stone are



thus leached, the more soluble compounds inward and the less soluble toward the surface, often forming a surface crust.

Sengupta and de Gast (1972) reported that  $\text{SO}_2$  sorption causes physical changes in stone involving changes in porosity and water retention. Removal of  $\text{CaCO}_3$  changes the physical nature of the stone surface. The hard, nonporous layer that forms as a result of alternate freezing and thawing may blister, exfoliate, and separate from the surface. If the stone contains some substances that are unaffected by  $\text{SO}_2$ , the surface can deteriorate unevenly. The conversion of  $\text{CaCO}_3$  to calcium sulfate results in a type of efflorescence called "crystallization spalling."

Baedecker et al. (1992) reported the results of a study on carbonate stone conducted as a part of National Acid Precipitation Assessment Program. Physical measurements of the recession of test stones exposed to ambient conditions at an angle of  $30^\circ$  to horizontal at 5 sites ranged from 15 to 30  $\mu\text{m}/\text{y}$  for marble and from 25 to 45  $\mu\text{m}/\text{y}$  for limestone and were approximately double the recession estimates based on the observed calcium content of run-off solutions from test slabs. The difference between the physical and chemical recession measurements was attributed to the loss of mineral grains from the stone surfaces that were not measured in the run-off experiments. The erosion due to grain loss did not appear to be influenced by rainfall acidity, however, preliminary evidence suggested that grain loss may be influenced by dry deposition of  $\text{SO}_2$  between rain events. Chemical analysis of the run-off solutions and associated rainfall blanks suggested 30% of erosion by dissolution could be attributed to the wet deposition of hydrogen ion and the dry deposition of  $\text{SO}_2$  and nitric acid between rain events. The remaining 70% of erosion by dissolution is accounted for by the solubility of carbonate stone in rain that is in equilibrium with atmospheric  $\text{CO}_2$  (clean rain). These results are for slabs exposed at  $30^\circ$  angles. The relative contribution of  $\text{SO}_2$  to chemical erosion was significantly enhanced for slab having an inclination of  $60^\circ$  to  $85^\circ$ . The dry deposition of alkaline particles at the two urban sites competed with the stone surface for reaction with acidic species.

Sweevers and Van Grieken (1992) studied the deterioration of sandstone, marble and granite under ambient atmospheric conditions. Specially constructed sampling devices, called "micro catchment units", were installed to sample the run-off water (i.e. the rain that flows over the stones). Several analysis techniques were invoked for the analysis of the bulk

runoff water, as well as electron probe X-ray microanalysis for individual particles in the runoff. There was a strong calcium to sulfate correlation on sandstone but not on granite after extended exposures.

Webb et al. (1992) studied the effects of air pollution on limestone degradation in Great Britain. There was a significant trend to increased weight loss with increased average  $\text{SO}_2$  concentration, but a negative trend with total  $\text{NO}_x$  and with  $\text{NO}_2$ . Rainfall did not significantly affect limestone degradation. Based on a mass and ion balance model, the natural solubility of limestone in water was the dominant term in describing the stone loss. The average overall recession rate was  $24 \mu\text{m/y}$ . The increase in stone loss due to  $\text{SO}_2$  was less than  $1 \mu\text{m/year/ppb}$ .

Butlin et al. (1992b) correlated damage to stone samples exposed at 29 monitoring sites in Great Britain. Portland limestone, White Mansfield dolomitic sandstone, and Monks Park limestone tablets ( $50 \times 50 \times 8 \mu\text{m}$ ) were exposed both under sheltered and unsheltered conditions. Weight change and ionic composition of surface powders were determined after one and two years of exposure.

The results showed the expected increases in acidic species and soluble calcium in the sheltered tablets. The stone deterioration data were statistically analyzed with respect to the environmental variables at the sites. Significant correlations existed between the mean annual  $\text{SO}_2$  concentration, rainfall volume, and hydrogen ion loading and the weight changes. These three correlations contain the three components that appear to be responsible for the degradation of calcareous stone, (1) dry deposition of acid gases and aerosols, (2) dissolution by acid species in rain water, and (3) the dissolution of stone by unpolluted rain water.

By analyzing storm runoff from a Vermont marble sample and comparing the results with the pollution exposure history, Schuster et al. (1994) have determined the relative contributions of wet and dry deposition to accelerated damage. Data were compared with runoff from glass for the same seven selected summer storms. Even though the exposure site had low concentrations of  $\text{SO}_2$ , it was estimated that between 10 and 50% of calcium washed from the marble surface during a storm was from the dissolution of gypsum formed by the reaction of  $\text{SO}_2$  during dry periods.

Yerrapragada et al. (1994) exposed samples of Carrara and Georgia marble for 6, 12, or 20 mo under normal atmospheric conditions. The samples were exposed outside, but

protected from the rain, at sites in Jefferson County, KY. These authors also analyzed samples of Georgia marble of varying ages from cemeteries in the Los Angeles basin. The researchers reported that  $\text{SO}_2$  is more reactive with the calcium in marble under higher  $\text{NO}_2$  conditions. The effects were noted even under relatively low  $\text{SO}_2$  and  $\text{NO}_2$  concentrations (10 to 20 and 22 to 32 ppb, respectively). Carrara marble was found to be more reactive with  $\text{SO}_2$  than Georgia marble, possibly due to the more compactness of the Georgia marble.

The effect of dry deposition of  $\text{SO}_2$ ,  $\text{NO}_2$ , and NO both with and without  $\text{O}_3$  on limestones and dolomitic sandstone was reported by Haneef et al. (1993). Samples of Portland limestone, Massamgis Jaune Roche limestone, and White Mansfield dolomitic sandstone were exposed to 10 ppm of each of the pollutants at a controlled relative humidity of 84% and a temperature of 292 °K. The stone samples were exposed to the controlled environment for 30 days. There was a small increase in sample weights after the 30 day exposure for all samples. Those samples exposed to  $\text{O}_3$  in addition to one of the other pollutants ( $\text{SO}_2$ ,  $\text{NO}_2$ , or NO) showed a significant increase in weight gain. All stone samples also showed retained sulfates or nitrates, particularly in the presence of  $\text{O}_3$ . When viewed by electron/optical techniques, a crust was noted on the surface and lining the pores of the stones exposed to  $\text{SO}_2$  but not those exposed to  $\text{NO}_2$  or NO.

Wittenburg and Dannecker (1992) measured dry deposition and deposition velocities of airborne acidic species on different sandstones. During different air-monitoring campaigns carried out in urban sites in East and West Germany, the dry deposition of particles and gaseous sulfur and nitrogen containing species on three different sandstones and on an inert substrate were measured. The measured depositions were related to the ambient air concentrations of the most important gaseous and particulate species. Dry deposition velocities were calculated and the proportions of particle and gas input depositions on the sandstones were estimated.

Salt accumulation in building stones was mainly caused by the gaseous components, especially  $\text{SO}_2$ . The deposition velocities were strongly dependent upon stone type. The contribution of sulfate particle deposition on sandstones was around 5 to 10% for vertical surfaces depending on the atmospheric conditions (Wittenburg and Dannecker, 1992).

Cobourn et al. (1993) used a continuing monitoring technique to measure the deposition velocity of  $\text{SO}_2$  on marble and dolomite stone surfaces in a humid atmosphere over a

2,000 ppm-h exposure period at approximately 10 ppm SO<sub>2</sub> and 100% relative humidity. The measured average deposition velocities of SO<sub>2</sub> over the two stones were comparable in magnitude. For dolomite, the measured deposition velocity varied between 0.02 and 0.10 cm/s, whereas for the marble, the deposition velocity varied between 0.03 and 0.23 cm/s. The measured deposition velocity for both types of stone changed as a function of time. The deposition velocity over dolomite increased gradually with time. The increase was attributed to a gradual increase of liquid water on the surface, brought about by the formation of the deliquescent mineral epsomite. The wide variation appeared to be associated with the absence or presence of condensed moisture on the marble sample surfaces. For most of the marble runs, the deposition velocity generally decreased slightly with time, after an initial period. The decrease could have been due to the build-up of reactions products on the stone surface.

Under high wind conditions, particles have been reported to result in slow erosion of marble surfaces, similar to sandblasting (Yocom and Upham, 1977). Mansfeld (1980), after performing statistical analysis of damage to marble samples exposed for 30 mo at 9 air quality monitoring sites in St. Louis, MO, concluded that exposure to TSP and nitrates were correlated with stone degradation. However, there is some concern over the statistical techniques used.

Generally, black and white areas can be observed on the exposed surfaces of any building. The black areas, found in zones protected from direct rainfall and from surface runs, are covered by an irregular, dendrite-like, hard crust composed of crystals of gypsum mixed with dust, aerosols, and particles of atmospheric origin. Among these the most abundant are black carbonaceous particles originating from oil and coal combustion. On the other hand, surfaces directly exposed to rainfall show a white color, since the deterioration products formed on the stone surface are continuously washed out.

The accumulation of gypsum on carbonate stone has been investigated by McGee and Mossotti (1992) through exposure of fresh samples of limestone and marble at monitored sites, examination of alteration crusts from old buildings, and laboratory experiments. McGee and Mossotti (1992) concluded that several factors contribute to gypsum accumulation on carbonate stone. Marble or limestone that is sheltered from direct washing by rain in an urban environment with elevated pollution levels is likely to accumulate a gypsum crust.

Crust development may be enhanced if the stone is porous or has an irregular surface area. Gypsum crusts are a superficial alteration feature; gypsum crystals form at the pore opening/air interface, where evaporation is greatest. Particles of dirt and pollutants are readily trapped by the bladed network of gypsum crystals that cover the stone surface, but the particles do not appear to cause the formation of gypsum crusts. Sabbioni and Zappia (1992) analyzed samples of damaged layers on marble and limestone monuments and historical buildings from 8 urban sites in Northern and Central Italy. Samples of black crust were taken from various locations at each site to be representative of the entire site. The predominant species in the black crust matrix was calcium sulphate dihydrate (gypsum). The evaluation of enrichment factors with respect to the stone and to the soil dust showed the main components of the atmospheric deposition to be from the combustion of fuels and incineration. Saiz-Jimenez (1993) also found, after analyzing the organic compounds extracted for black crusts removed for building surfaces in polluted areas, that the main components were composed of molecular markers characteristic of petroleum derivatives. The composition of each crust, however, is governed by the composition of the particular airborne pollutants in the area.

Sabbioni et al. (1992) conducted a laboratory study on the interaction between carbonaceous particles and carbonate building stones. Three types of building stones with the common characteristic of a carbonate matrix were used: (1) Carrar marble, (2) Travertine, and (3) Trani stone. Samples of the emissions from two oil-combustion sources, representative of a centralized domestic heating system and an electric generating plant, were characterized by means of chemical and physical analysis and spread manually on the stone samples. Any excess was removed using compressed air. The distribution of the particles on the surface of the samples was controlled by optical microscopy. The stone samples were weighed before and after the particle deposition. Stones without particles were also exposed as reference samples. The samples with particles containing the highest carbon content had the lowest reactivity in the sulfation process. Particles with high sulphur content enhanced the reactivity of the stone samples with SO<sub>2</sub> (Sabbioni et al., 1992).

Del Monte et al. (1981) reported evidence of a major role for carbonaceous particles in marble deterioration, using scanning electron microscopy. The majority of the carbonaceous

particles were identified as products of oil fired boiler/combustion. Particle median diameter was  $\approx 10 \mu\text{m}$ .

Delopoulou and Sikiotis (1992) compared the corrosive action of nitrates and sulfates on pentelic marble with that of  $\text{NO}_x$  and  $\text{SO}_2$ . This was achieved by passing the polluted ambient air through a filter pack before it entered the reactor chamber holding the marble grains. As a consequence, the air reaching the marble was free of nitrates and sulfates while it contained all the  $\text{NO}_x$  and  $\text{SO}_2$ . The effects on the marble grains were quantified and compared with those from a reactor through which unfiltered ambient air was passed simultaneously and under the same conditions. They reported that the action of the acids was much greater than that of the oxides, despite the fact that the concentrations of the latter were much greater.

### **9.1.6 Corrosive Effects of Acid-Forming Aerosols and Particles on Other Materials**

Exposure to ionic dust particles can contribute significantly to the corrosion rate of electronic devices, ultimately leading to failure of such device. Anthropogenically and naturally derived particles ranging in size from tens of angstroms to  $1 \mu\text{m}$  cause corrosion of electronics because many are sufficiently hygroscopic and corrosive at normal relative humidities to react directly with non-noble metals and passive oxides, or to form sufficiently conductive moisture films on insulating surfaces to cause electrical leakage. The effects of particles on electronic components were first reported by telephone companies, when particles high in nitrates caused stress corrosion cracking and ultimate failure of the wire spring relays (Hermance, 1966; McKinney and Hermance, 1967). More recently, attention has been directed to the effects of particles on electronic components, primarily in the indoor environment.

Sinclair (1992) discussed the relevance of particle contamination to corrosion of electronics. Data collected during the 1980s show that the indoor mass concentrations of anthropogenically derived airborne particles and their arrival rates at surfaces are comparable to the concentrations and arrival rates of corrosive gases for many urban environments.

Frankenthal et al. (1993) examined the effects of ionic dust particles, ranging from 0.01 to  $1 \mu\text{m}$  in size, on copper coupons under laboratory conditions. The copper coupons,

after being polished with diamond paste, were inoculated with ammonium sulfate  $[(\text{NH}_4)_2\text{SO}_4]$  particles and exposed to air at 100 °C and relative humidities ranging from 65 to 100% for up to 600 h. The particles were deposited on the metal surface by thermophoretic deposition and cascade impaction.

Exposure of the copper coupons to  $(\text{NH}_4)_2\text{SO}_4$  at 65% relative humidity had little effect on the corrosion rate. However, when the relative humidity was increased to 75%, the critical relative humidity for  $(\text{NH}_4)_2\text{SO}_4$  at 100 °C, localized areas of corrosion were noted on the metal surface. The corrosion product, determined to be brochantite, was only found in areas where the  $(\text{NH}_4)_2\text{SO}_4$  was deposited on the metal surface. When relative humidity was increased to 100%, the corrosion became widespread (Frankenthal et al., 1993).

## 9.2 SOILING AND DISCOLORATION

A significant detrimental effect of particle pollution is the soiling of manmade surfaces. Soiling may be defined as a degradation mechanism that can be remedied by cleaning or washing, and depending on the soiled material, repainting. Faith (1976) described soiling as the deposition of particles of less than 10  $\mu\text{m}$  on surfaces by impingement. Carey (1959) observed when particles descended continuously onto paper in a room with dusty air, the paper appeared to remain clean for a period of time and then suddenly appeared dirty. Increased frequency of cleaning, washing, or repainting over soiled surfaces becomes an economic burden and can reduce the life usefulness of the material soiled. In addition to the aesthetic effect, soiling produces a change in reflectance from opaque materials and reduces light transmission through transparent materials (Beloin and Haynie, 1975; National Research Council, 1979). For dark surfaces, light colored particles can increase reflectance (Beloin and Haynie, 1975).

Determining at what accumulated level particle pollution leads to increased cleaning is difficult. For instance, in the study by Carey (1959), it was found that the appearance of soiling only occurred when the surface of the paper was covered with dust specks spaced 10 to 20 diameters apart. When the contrast was strong, e.g., black on white, it was possible to distinguish a clean surface from a surrounding dirty surface when only 0.2% of the areas was covered with specks, while 0.4% of the surface had to be covered with specks

with a weaker color contrast. Still, the effect is subjective and not easy to judge between coverages.

Support for the Carey (1959) work was reported by Hancock et al. (1976). These authors also found that with maximum contrast, a 0.2% surface coverage (effective area coverage; EAC) by dust can be perceived against a clean background. A dust deposition level of 0.7% EAC was needed before the object was considered unfit for use. The minimum perceivable difference between varying gradations of shading was a change of about 0.45% EAC. Using the information on visually perceived dust accumulation and a telephone survey, Hancock et al. (1976) concluded that a dustfall rate of less than 0.17% EAC/day would be tolerable to the general public.

Some materials that are soiled are indoors. In general, particle pollution levels indoors may be affected by outdoor ambient levels; however, other factors generally have greater effects on concentration and composition (Yocom, 1982). For that reason, discussion of indoor soiling will be limited primarily to works of art.

### **9.2.1 Building Materials**

Dose-response relationships for particle soiling were developed by Beloin and Haynie (1975) using a comparison of the rates of soiling and TSP concentrations on different building materials (painted cedar siding, concrete block, brick, limestone, asphalt singles, and window glass) at 5 different study sites over a 2-y period. Particle concentrations ranged from 60 to 250 mg/m<sup>3</sup> for a rural residential location and an industrial residential location, respectively. The results were expressed as regression functions of reflectance loss (soiling) directly proportional to the square root of the dose. With TSP expressed in mg/m<sup>3</sup> and time in months, the regression coefficients ranged from -0.11 for yellow brick to +0.08 for a coated limestone depending on the substrate color and original reflectance. For dark surfaces, light colored particles can increase reflectance. Not all of the coefficients were significantly different from zero.

A theoretical model of soiling of surfaces by airborne particles has been developed and reported by Haynie (1986). This model provides an explanation of how ambient concentrations of particulate matter are related to the accumulation of particles on surfaces and ultimately the effect of soiling by changing reflectance. Soiling is assumed to be the



contrast in reflectance of the particles on the substrate to the reflectance of the bare substrate. Thus, the average reflectance from the substrate ( $R$ ) equals the reflectance from the substrate not covered by particles [ $R_o(1-X)$ ] plus the reflectance from the particles ( $R_pX$ ) where  $X$  is the fraction of surface covered by particles.

Under constant conditions, the rate of change in fraction of surface covered is directly proportional to the fraction of surface yet to be covered. Therefore, after integration:  $X = 1 - \exp(-kt)$  where  $k$  is a function of particle size distribution and dynamics and  $t$  is time. Lanting (1986) evaluated similar models with respect to soiling by particulate elemental carbon (PEC) in the Netherlands. He determined that the models were good predictors of soiling of building materials by fine mode black smoke. Based on the existing levels of PEC, he concluded that the cleaning frequency would be doubled.

An important particle dynamic is deposition velocity which is defined as flux divided by concentration and is a function of particle diameter, surface orientation, and surface roughness, as well as other factors such as wind speed, atmospheric stability, and particle density. Thus, soiling is expected to vary with the size distribution of particles within an ambient concentration, whether a surface is facing skyward (horizontal versus vertical), and whether a surface is rough or smooth.

Van Aalst (1986) reviewed particle deposition models existing at that time and pointed out both their benefits and their faults. The lack of significant experimental verification was a major fault. Since then, Hamilton and Mansfield (1991, 1993) have applied the model reported by Haynie (1986) and Haynie and Lemmons (1990) to soiling experiments with relatively good predictive success.

Terrat and Joumard (1990) found that the simple plate method (a measurement of the number of particles deposited on a flat inert plate of material), as well as the measurement of reflectance and transmission of the light really showed the amount of soiling deposit in a town. The simple plates are more suitable for high particle polluted areas and the optical methods are more suitable for low pollution areas. This study also provided evidence that motor vehicles are mainly responsible for soiling the facades along roads.

### **9.2.1.1 Fabrics**

No recent information on the effects of particles on fabrics was located in the published literature. Earlier studies indicate particles are only damaging to fabrics when they are abrasive. Yocom and Upham (1977) reported that curtains hanging in an open window often split in parallel lines along the fold after being weakened by particle exposure. The appearance and life usefulness also may be lessened from increased frequencies of washing as a result of particle "soiling". Rees (1958) described the mechanisms (mechanical, thermal, and electrostatic) by which cloth is soiled. Tightly woven cloth exposed to moving air containing fine carbon particles was found to be the most resistant to soiling. Soiling by thermal precipitation was related to the surface temperature of the cloth versus that of the air. When the surface temperature of the cloth was greater than that of the air, the cloth resisted soiling. When cloth samples were exposed to air at both positive and negative pressure, the samples exposed to positive pressure showed greater soiling than those exposed to equivalent negative pressure.

### **9.2.1.2 Household and Industrial Paints**

Research suggest that particles can serve as carriers of more corrosive pollutants, allowing the pollutants to reach the underlying surface or serve as concentration sites for other pollutants on painted surfaces (Cowling and Roberts, 1954). Paints may also be soiled by liquids and solid particles composed of elemental carbon, tarry acids, and various other constituents.

Haynie and Lemmons (1990) conducted a soiling study at an air monitoring site in a relatively rural environment in Research Triangle Park, NC. The study was designed to determine how various environmental factors contribute to the rate of soiling of white painted surfaces. White painted surfaces are highly sensitive to soiling by dark particles and represent a large fraction of all manmade surfaces exposed to the environment. Hourly rainfall and wind speed, and weekly data for dichotomous sampler measurements and TSP concentrations were monitored. Gloss and flat white paints were applied to hardboard house siding surfaces and exposed vertically and horizontally for 16 weeks, either shielded from or exposed to rainfall. Particle mass concentration, percentage of surfaces covered by fine and coarse mode fractions, average wind speed and rainfall amounts, and paint reflectance

changes were measured at 2, 4, 8, and 16 weeks. The scanning electron microscopy stubs, that had been flush-mounted on the hardboard house siding prior to painting, were also removed and replaced with unpainted stubs at these intervals.

The unsheltered panels were initially more soiled by ambient pollutants than the sheltered panels; however, washing by rain reduced the effect. The vertically exposed panels soiled at a slower rate than the horizontally exposed panels. This was attributed to additional contribution to particle flux from gravity. The reflectivity was found to decrease faster on glossy paint than on the flat paint (Haynie and Lemmons, 1990).

Least squares fits through zero of the amounts on the surfaces with respect to exposure doses provided the deposition velocities. There was no statistical difference between the horizontal and vertical surfaces for the fine mode and the combined data given a deposition velocity of  $0.00074 + 0.000048 \text{ cm/s}$  (which is lower than some reported values). The coarse mode deposition velocity to the horizontal surfaces at  $1.55 \text{ cm/s}$  is around five times greater than to vertical surfaces at  $0.355 \text{ cm/s}$ . By applying assumptions these deposition velocities can be used to calculate rates of soiling for sheltered surfaces. The empirical prediction equation for gloss paint to a vertical surface based on a theoretical model (Haynie, 1986) is:

$$R = R_0 \exp (-0.0003[0.0363C_f + 0.29C_c]t) \quad (9-8)$$

where  $R$  and  $R_0$  are reflectance and original reflectance, respectively,  $C_f$  and  $C_c$  are coarse and fine mode particle concentrations in  $\mu\text{g}/\text{m}^3$ , respectively, and  $t$  is time in weeks of exposure.

The fine mode ( $<2.5 \mu\text{m}$ ) did not appear to be washed away by rain, but most of the coarse mode ( $>2.5 \mu\text{m}$  to  $10 \mu\text{m}$ ) was either dissolved to form a stain or was washed away. Therefore, for the surfaces exposed to rain, the 0.0363 coefficient for the fine mode should remain the same as it is for sheltered surfaces but there should be a time-dependent difference in the coefficient for the coarse mode.

Based on the results of this study, the authors concluded that: (1) coarse mode particles initially contribute more to soiling of both horizontal and vertical surfaces than fine mode

particles; (2) coarse mode particles, however, are more easily removed by rain than are fine mode particles; (3) for sheltered surfaces reflectance changes is proportional to surface coverage by particles, and particle accumulation is consistent with the deposition theory; (4) rain interacts with particles to contribute to soiling by dissolving or desegregating particles and leaving stains; and (5) very long-term remedial actions are probably taken because of the accumulation of fine rather than coarse particles (Haynie and Lemmons, 1990).

Similar results were also reported by Creighton et al. (1990). They found that horizontal surfaces, under the test conditions, soiled faster than did the vertical surfaces, and that large particles were primarily responsible for the soiling of horizontal surfaces not exposed to rainfall. Soiling was related to the accumulated mass of particles from both the fine and coarse fractions. Exposed horizontal panels stain because of dissolved chemical constituents in the deposited particles. The size distribution of deposited particles was bimodal, and the area of coverage by deposited particles was also bimodal with a minimum at approximately  $5\ \mu\text{m}$ . The deposition velocities for each of the size ranges onto the horizontal, sheltered panel was in general agreement with both the theoretical settling velocity of density  $2.54\ \text{g/cm}^3$  spheres and the reported results of laboratory tests. An exponential model (Haynie, 1986) was applied to the data set and gave a good fit.

Spence and Haynie (1972) reported on the published data on the effects of particles on the painted exterior surfaces of homes in Steubenville and Uniontown, OH, Suitland and Rockville, MD, and Fairfax, VA. There was a direct correlation between the ambient concentration of particulate matter in the city and the number of years between repainting. The average repainting time for homes in Steubenville, where particulate matter concentrations averaged  $235\ \mu\text{g/m}^3$ , was approximately one year. In the less polluted city, Fairfax, where the particulate matter concentrations only reached  $60\ \mu\text{g/m}^3$  (arithmetic means), the time between repainting was 4 years. Parker (1955) reported the occurrence of black specks on the freshly paint surface of a building in an industrial area. The black specks were not only aesthetically unappealing, but also physically damaged the painted surface. Depending on the particle concentration, the building required repainting every 2 to 3 years.

### **9.2.1.3 Soiling of Works of Art**

Ligocki et al. (1993) studied potential soiling of works of art. The concentrations and chemical composition of suspended particles were measured in both the fine and coarse size modes inside and outside five Southern California museums during summer and winter months. The seasonally averaged indoor/outdoor ratios for particle mass concentrations ranged from 0.16 to 0.96 for fine particles and from 0.06 to 0.53 for coarse particles, with lower values observed for buildings with sophisticated ventilation systems that include filters for particle removal. Museums with deliberate particle filtration systems showed indoor fine particle concentrations generally averaging less than  $10 \mu\text{g}/\text{m}^3$ . One museum with no environmental control system showed indoor fine particles concentrations averaging nearly  $60 \mu\text{g}/\text{m}^3$ . Analysis of indoor versus outdoor concentrations of major chemical species indicated that indoor sources of organics may exist at all sites, but that none of the other measured species appear to have major indoor sources at the museums studied. The authors concluded that a significant fractions of the dark-colored fine elemental carbon and soil dust particles present in the outdoor environment had penetrated to the indoor atmosphere of the museums studied and may constitute a soiling hazard to displayed works of art.

Methods for reducing the soiling rate in museums that included reducing the building ventilation rate, increasing the effectiveness of particle filtration, reducing the particle deposition velocity onto surfaces of concern, placing objects within display cases or glass frames, managing a site to achieve lower outdoor aerosol concentrations, and eliminating indoor particle sources were proposed by Nazaroff and Cass (1991). According to model results, the soiling rate can be reduced by at least two orders of magnitude through practical application of these control measures. Combining improved filtration with either a reduced ventilation rate for the entire building or low-air-exchange display cases would likely reduce the soiling hazard in museums.

## **9.3 ECONOMIC ESTIMATES**

Only limited new information was located in the published literature on the economic cost of soiling and corrosion by particles. Many of these studies are flawed or represent monetary cost for materials damage and soiling that are not representative of monetary losses

today. A detailed discussion of earlier studies on economic loss from exposure to acid forming aerosols and other particles can be found in the previous criteria document for particulate matter (U.S. Environmental Protection Agency, 1982). The following sections describe methods for determining economic losses from materials damage and soiling from air pollution and includes the limited body of new information available since publication of the 1982 particulate matter criteria document.

### **9.3.1 Methods for Determining Economic Loss from Pollutant Exposure**

Several types of economic losses result from materials damage and soiling. Financial or out-of-pocket losses include the reduction in service life of a material, decreased utility, substitution of a more expensive material, losses due to an inferior substitute, protection of susceptible materials, and additional required maintenance, including cleaning. The major losses of amenity, as defined by Mäler and Wyzga (1976), are associated with enduring and suffering soiled, damaged, or inferior products and materials because of particle pollution and any corrosive pollutant that may be absorbed on or adsorbed to particles. In addition, amenity losses are suffered when pollution damage repair or maintenance procedures result in inconvenience or other delays in normal operations. Some of these losses, such as effects on monuments and works of art, are especially difficult to specify (Mäler and Wyzga, 1976).

The compilation and assessment of materials damage and soiling research reveals a variety of techniques employed by different disciplines to estimate economic losses associated with soiling and materials damage. Attempts have been made to address the following questions.

- At what concentration or deposition rate is materials damage and soiling perceived?
- What is the relationship between the color of the particle and perceived materials damage and soiling?
- What is the physical or economic life of various materials, coatings, structures, etc.?
- What is the inventory of pollution sensitive materials, coatings, structures, etc.?
- What behaviors are undertaken to avert, mitigate, or repair pollution-related damages?

- What is the economic cost of materials damage and soiling due to exposure to acid forming aerosols and other particles?

The answers to these questions are certainly relevant to the structure of a modeling framework, the collection of data, and the estimation of effects of materials damage and soiling on economic values. The analytical approach selected depends on whether financial losses or losses of amenity are emphasized, the type of damage being considered, and the availability of cost information. Economic losses from pollutant exposure can be estimated using the damage function approach or using direct economic methods.

In the damage function approach, physical damage (any undesirable change in the function of specific materials, including appearance, leading to failure of specific components) is determined before economic cost is estimated. Physical damage is estimated from ambient pollutant concentrations over a specified period of time. Depending on the material damaged, both short-term and long-term exposure data may be necessary to determine a more accurate estimate of damage related to pollution exposure. The damage function is expressed in terms appropriate to the interaction of the pollutant and material. For example, the corrosion of metal may be expressed in units of thickness lost, while the deterioration of paint from soiling may be expressed in units of reflectance lost. A willingness-to-pay value, mitigation, or replacement cost is then applied to estimate a monetary value of damages caused by changes in pollutant concentrations. It is, however, difficult to estimate fully the financial losses because reliable information is not available on the physical damage of all economically important materials, and on the spatial and temporal distribution of these materials. Further, current techniques do not reflect the use of more resistant and reduced-maintenance materials, and loss estimates may assume that substitute materials cost more than the original materials, and that the cost differential is attributable solely to pollution.

Another major problem in developing reliable damage functions is the inability to separate pollutant effects from natural weathering processes due to various meteorological parameters (temperature, relative humidity, wind speed, and surface wetness). Since weathering is a natural phenomenon, proceeding at a finite rate irrespective of anthropogenic pollution, materials damage estimates must represent only that damage directly produced by

anthropogenic pollutant exposure. Also, this approach cannot account for irreplaceable items such as works of art or national monuments.

In the studies that do not use the physical damage approach to derive monetized economic damages reflecting the estimates of damages associated with pollution, the loss of amenity or direct financial losses are estimated econometrically. These approaches have been used to relate changes in air pollution directly with the economic value of avoidance or mitigation of damages. A major source of error using these approaches is the requirement that all factors that affect cost other than air quality have to be accounted for. In general all approaches to estimating costs of air pollution effects on materials are limited by the difficulty in quantifying the human response to damage based upon the ability and the incentive to pay additional costs (Yocom and Grappone, 1976).

### **9.3.2 Economic Loss Associated with Materials Damage and Soiling**

Information on the geographic distribution of various types of exposed materials may provide an indication of the extent of potential economic costs of damage to materials from air pollution. Lipfert and Daum (1992) analyzed the efforts made to determine the geographic distribution of various types of materials. They focused on the identification, evaluation and interpretation of data describing the distribution of exterior construction materials, primarily in the United States. Materials distribution surveys for 16 cities in the United States and Canada and five related data bases from government agencies and trade organizations were examined. Data on residential buildings were more available than non-residential buildings; little geographically resolved information on distributions on materials in infrastructure was found.

Lipfert and Daum (1992) observed several important factors relating pollution to distribution of materials. In the United States, buildings constitute the largest category of surface areas potentially at risk to pollution damage. Within this category, residential buildings are the most important. On average, commercial and industrial buildings tend to be larger than residential buildings and to use more durable materials. However, because they are more numerous (and use less durable materials) more surface area for residential buildings is exposed to potentially damaging pollutants. For residential buildings in general, painted surfaces are preferred over masonry in the Northeastern United States (with the

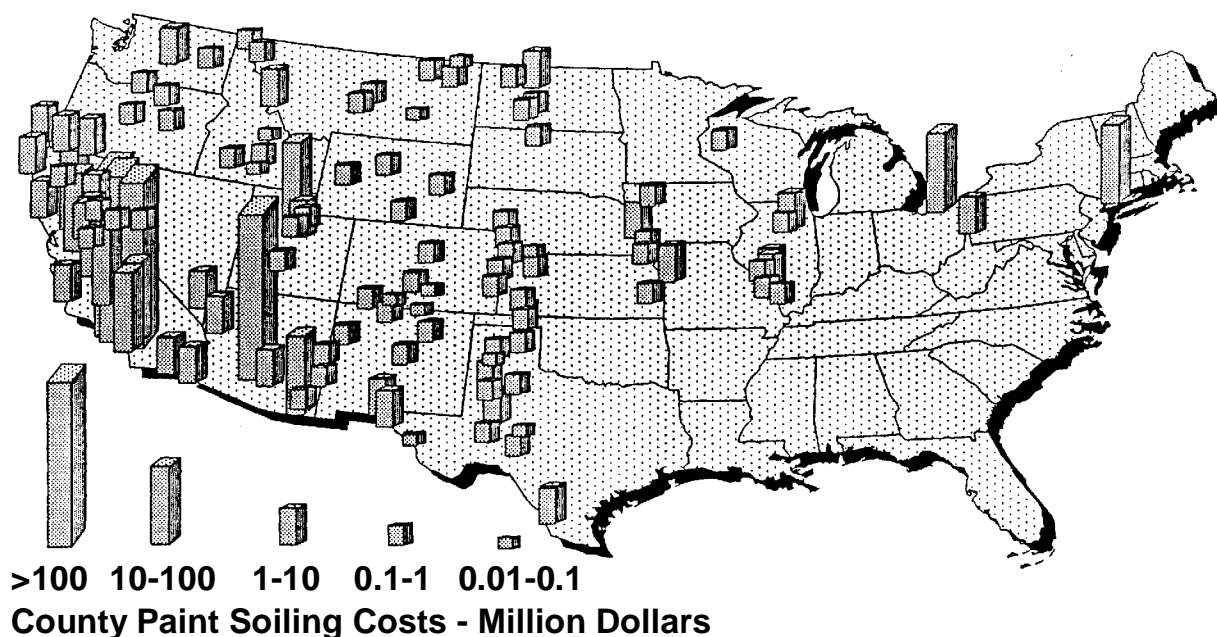


exception of large inner cities), brick is popular in the South and Midwest) and stucco in the West. The use of brick appears to be declining, painted wood increasing, and the use of vinyl siding is gaining over aluminum. One of the factors underlying the present regional distribution of materials is their durability under the environmental conditions which exist when they were installed. Thus, changing pollution levels have possibly affected materials selection, and is expected to do so.

Haynie (1990) examined the potential effects of  $PM_{10}$  nonattainment on the costs of repainting exterior residential walls due to soiling in 123 counties. The analysis was based on a damage function methodology developed for a risk assessment of soiling of painted exterior residential walls (Haynie, 1989). The data base was updated with 1988 and 1989 AIRS data. An extreme value statistical model was used to adjust every sixth day monitoring to 365 days for counting violation days (one violation in 60 does not translate to 6 violations in 360). The resulting paint cost due to soiling was subjected to a sensitivity analysis using various assumed values. When the model is restricted to only a national average of 10% of households repainting because of soiling, the effects of other assumptions become inversely related and tend to cancel out each other (possibly associated with individual cost minimization choices).

The top twenty counties were ranked by estimated soiling costs. Fourteen of the counties with actual violation days in 1989 were in this group. All but three were west of the Mississippi. A total of 29 counties with measured violations are in the set of 123 counties for which  $PM_{10}$  nonattainment soiling costs were calculated. When the given set of behavior assumptions was used, there were no costs calculated for 19 counties that actually measured violations in 1989. The distribution of a national estimated \$1 billion in painted exterior residential wall soiling costs is shown in Figure 9-2.

An experimentally determined soiling function for unsheltered, vertically exposed house paint was used to determine painting frequency (Haynie and Lemmons, 1990). An equation was set up to express paint life in integer years because the painting of exterior surfaces is usually controlled by season (weather). Different values for normal paint life without soiling and levels of unacceptable soiling could be used in the equation. If four was taken as the most likely average paint life for other than soiling reasons, then painting because of soiling would likely be done at 1, 2, or 3 year intervals.



**Figure 9-2. Geographic distribution of paint soiling costs.**

Source: Haynie (1990).

Soiling costs by county were calculated and ranked by decreasing amounts and the logarithm of costs plotted by rank. The plot consisted of three distinct straight lines with intersections at ranks 4 and 45. The calculated cost values provide a reasonable ranking of the soiling problem by county, but do not necessarily reflect actual painting cost associated with extreme concentrations of particles. Households exposed to extremes are not expected to respond with average behavior. The authors concluded that repainting costs could be lowered if: (1) individuals can learn to live with higher particle pollution, accepting greater reductions in reflectance before painting; (2) painted surfaces were washed rather than repainted; and (3) if materials or paint colors that do not tend to show dirt were used.

Extrapolating the middle distribution of costs to the top four ranked counties reduces their estimated costs considerably. For example Maricopa County, AR, was calculated to rank first at \$70.2 million if all households painted each year as predicted, but was calculated to be only \$29.7 million based on the distribution extrapolation.

Based on these calculations and error analysis, the national soiling costs associated with repainting the exterior walls of houses probably were within the range of \$400 to \$800 million a year in 1990. This sector represents about 70% of the exterior paint market, so that extrapolating to all exterior paint surfaces gives a range of from \$570 to \$1,140 million (Haynie and Lemmons, 1990).

A number of other studies have attempted to model the economic losses of soiling due to particulate air pollution. Based on the hypothesis that air pollution affects the budget allocation decisions of individuals, MathTech (1983) used a household sector model to establish a statistical relationship between TSP and the demand for laundry and cleaning products and services using 1972-1973 Bureau of Labor Statistics Consumer Expenditure data. Given knowledge of the pattern of demand for these goods, standard methods of welfare economics were used to estimate the benefits (or compensating variation) of changes in TSP concentrations. The results of this study indicated that the annual benefits of attaining the primary  $PM_{10}$  standard were approximately \$88.3 million to \$1.2 billion in 1980 dollars for the period 1989 to 1995. The applicability of the underlying relationship to current air quality and economic conditions is uncertain given that potential changes in consumer tastes and the opportunity set of goods influencing budget allocation decisions could have changed over the intervening 20 years.

MathTech (1990) also assessed the effects of acidic deposition on painted wood surfaces using individual maintenance behavior data. The effects were a function of the repainting frequency of the houses as well as pollution levels.

Gilbert (1985) used a household production function framework to design and estimate the short-run costs of soiling. The results were comparable to those reported by MathTech (1983). Smith and Gilbert (1985) also used a hedonic property value model to analyze the effects of particles in the long term, examining the possibility of households moving in response to air pollution.

McClelland et al. (1991) conducted a field study valuing eastern visibility using the contingent valuation method. Given the problem of embedding between closely associated attributes, the survey instrument provided for separation of the visibility, soiling, and health components of the willingness-to-pay estimates. Households were found to be willing to pay \$2.70 per  $\mu g/m^3$  change in particle pollution to avoid soiling effects.

The findings of the aforementioned studies are consistent with the hypotheses that there are economic costs associated with elevated pollution levels across multiple sectors and that households are willing to pay positive amounts to reduce particle concentrations to reduce the risk of materials damage and soiling. However, these studies have done little to advance our knowledge of perception thresholds in relationship to concentration, particle size, and chemical composition. Without such information it is very difficult and highly uncertain to quantify the relationship between ambient particle concentrations and soiling and associated economic cost.

## **9.4 SUMMARY**

Available information supports the fact that exposure to acid forming aerosols promotes the corrosion of metals beyond the corrosion rates expected from exposure to natural environmental elements (wind, rain, sun, temperature fluctuations, etc.). Many metals form a protective film that protects against corrosion; however, high concentrations of anthropogenic pollutants, lessen the effectiveness of the protective film. Acid forming aerosols have also been found to limit the life expectancy of paints by causing discoloration, loss of gloss, and loss of thickness of the paint film layer.

Various building stones and cement products are damaged from exposure to acid-forming aerosols. However, the extent of the damage to building stones and cement products produced by the pollutant species, beyond that expected as part of the natural weathering process is uncertain. Several investigators have suggested that the damage attributed to acid forming pollutants is overestimated and that stone damage is predominantly associated with relative humidity, temperature, and, to a lesser degree, air pollution.

A significant detrimental effect of particle pollution is the soiling of painted surfaces and other building materials. Soiling is defined as a degradation mechanism that can be remedied by cleaning or washing, and depending on the soiled surface, repainting. Available data on pollution exposure indicates that particles can result in increased cleaning frequency of the exposed surface, and may reduce the life usefulness of the material soiled. Data on the effects of particulate matter on other surfaces are not as well understood. Some evidence does, however, suggest that exposure to particles may damage fabrics, electronics, and works

of art composed of one or more materials, but this evidence is largely qualitative and sketchy.

The damaging and soiling of materials by acid forming aerosols and other particles have an economic impact, but this impact is difficult to measure. One problem is the lack of sufficient data to separate costs between various pollutants and to separate cost of pollutant exposure from that of normal maintenance. Attempts have been made to quantify the pollutants exposure levels at which materials damage and soiling have been perceived. However, to date, insufficient data are available to advance our knowledge regarding perception thresholds with respect to pollutant concentration, particle size, and chemical composition.

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